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INFLUENCE OF TEMPERATURE, SALINITY, AND SALT EFFECT FOR DISPERSION OF OIL BY LECITHIN BLENDS ON SEAWATER

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ABSTRACT

Treatment of oil spill disasters is until challenging concept in which the application of chemical dispersant is one of the accepted oil spill responses on a global level. Nowadays, its toxicity is also concerned regarding the survival of seawater ecosystems. This can be depressed by designing eco-friendly formulations of dispersants with their application in majorly all the water bodies having different environmental parameters like temperature, salinity, salt content, etc. In this study, Lecithin blended with Tween derivatives having different Hydrophilic-Lipophilic Balance (HLB) applied on the dispersion of High-density oil. Temperature (15oC - 40OC) and salinity (34ppt and 36ppt) were applied for this study. NaCl, Na2SO4, and Na-benzoate, MgSO4, MgCl2 salts with artificial sea salt were used to compare the dispersion effectiveness of these blends. The interfacial activity and FT-IR of the formulated dispersants were also examined. With the US EPA's baffled flask test, lecithin-blends resulted in near-complete dispersion effectiveness. Salinity has a significant role ($p < 0.05$) to disperse the oil in seawater. Magnesium salts recorded more significant values ($p < 0.05$) regarding dispersant effectiveness of lecithin blends as compared to Sodium. The dispersion of oil in seawater rapidly forwarded by selecting such dispersants affected by the salt effect.

KEYWORDS: Dispersant Effectiveness, Lecithin, Oil Spill, Salinity, Salt Effect

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Original Article

1. INTRODUCTION

The ocean is contaminated due to kinds of impurities, in which oil spills have been the topmost contributors as there is the rapid development of offshore oil exploration technologies and marine transportation with severe accidents (Naser, 2013). There are sorts of treatments that are employed to negotiate the hazardous effects of oil spills depending upon the varying conditions. One of the most acceptable and applicable response measures is oil spill dispersants with varying types and concentrations (Al-Majed *et al*, 2012). Hence, rectifying the lethal effects of oil spill dispersant has become a preferential impetus than ever before (Prince, 2015). To overcome the toxic effects of dispersants upon application, several formulations have been designed. These updated dispersants consist of halloysite nanotubes as vehicles for dispersants (Owoseni *et al*, 2014; Nyankson *et al*, 2015; Owoseni *et al*, 2016), dispersant composite particles (Nyankson *et al*, 2014), and soybean in dispersant formulation (Nyankson *et al*, 2016).

Various studies have been conducted regarding the efficiency of Soybean lecithin in dispersing crude oil, which confirmed that its effectiveness was moreover than many of the traditionally formulated dispersants (Nyankson *et al*, 2015). Furthermore, it should consider that factors as if salinity, temperature, salts of seawater modify the dispersant efficiency of dispersant formulations and their combinations (Chapman et al, 2007). At the oil-water interface, adsorption of soybean lecithin formulated dispersant having an ionic head group of

phospholipids has expected to influence. In the formation of stable emulsion, it can be crucial for ionic surfactants at the oil-water interface to the adsorption behavior by the presence of salt. The salting-out phenomenon is forwarded when there is the blending of ionic surfactants and salts in an aqueous solution (Mukerjee *et al,* 2002; Wattebled *et al,* 2007). According to reports, it has stated that, at the fluid-fluid interface, inorganic salts have a significant effect on the volume of surfactant adsorbed. The electrostatic repulsion among the surfactants head groups alters by added inorganic salts, which put forth a significant reduction in the surface tension. Many reports stated that reduction of surface tension is to be dependent on the valency of cations having in the inorganic salts (Giribabu *et al*, 2007). In aqueous solutions, along with electrostatic interactions, organic salts exhibit hydrophobic interactions with ionic salts, which results in tight packing at the oil droplet-water interface (Shikata *et al,* 1998). There are few studies on the effect of organic and inorganic salts on the interfacial characteristics of soybean lecithin surfactant in the literature. Therefore, the results from this study will help to predict the efficiency of chemical dispersant application for the treatment of oil spills.

In this study, the effect of magnesium and sodium salts on the interfacial characteristics of soybean lecithin dispersant was examined. The sodium salts used in this study were sodium chloride (NaCl), sodium sulfate (Na_2SO_4), and sodium benzoate (Na-benzoate). The magnesium salts used were magnesium chloride ($MgCl_2$) and magnesium sulfate ($MgSO_4$). The major reason to select the Sodium and Magnesium salts, that they form the main constituents in seawater. Lecithin is a food-grade amphiphile blended with non-ionic dispersants such as Tween 85 and Tween 80 with 7:3 concentration ratios. The effect of the different salts on the dispersion effectiveness of lecithin blends was examined using the U.S. EPA's baffled flask test (Sorial *et al*, 2004I; Sorial *et al,* 2004II; Venosa *et al*, 2002). The artificial salt was kept as a control for this experiment. The whole experiment was conducted at a temperature range from 15ºC to 40ºC (at a 5ºC interval) and salinity concentrations 34ppt and 36ppt.

The interfacial tension of Lecithin blends was measured by a Tensiometer (Pendant Drop method). FT-IR analysis was carried out to measure active functional groups of blends. Statistical Analysis was performed for testing the results. (Two-Way ANOVA, SPSS, 2016)

2. MATERIALS AND METHODS

2.1 Materials

Soybean lecithin was purchased from Amrut Industrials (Mumbai) and absolute ethanol (95%) was obtained from Thermo-Fischer. Sodium chloride, magnesium chloride, sodium sulfate, sodium benzoate, magnesium sulfate were obtained from Sigma-Aldrich. Dichloromethane (75-09-2) was purchased from Thermo-Fischer. The high-density oil used in this study. Artificial Sea salt was purchased from Taiyo Pvt. Ltd. (Chennai) Two Salt solutions of 3.4wt.% and 3.6wt.% concentrations were prepared by dissolving 34g and 36g of the salt in distilled water (1L). The resulting salt solutions are used as the synthetic seawater/salt solution in this study.

2.2 Characterization of Substrate

For the surface tension, a known amount of the solubilized lecithin was added to a known volume of the Tween derivatives with alcohol as a solvent. A drop of these samples was quickly injected from a syringe. The dynamic surface tension was measured by a drop shape analysis using the DROP image Advanced Software (Tensiometer) (Dept. of Physics, SPPU, Pune). FT-IR analysis was carried out on Shimadzu FT-IR (Dept. of Chemistry, Radhabai Kale Women's College, Ahmednagar).

2.3 Dispersion Effectiveness Determination

The dispersion effectiveness of the lecithin blends in various saltwater solutions was determined using the baffled flask test. 100μL of high-density oil added to 120 mL of synthetic seawater in a baffled flask. A known volume (1:25 ratio) of the solubilized lecithin blend was added directly on top of the high-density oil, and the baffled flask was placed on an orbital shaker set at 200 rpm for 2hrs with triplicates. The whole study was carried out at a temperature range from 15°C to 40°C. After 10 min, it was allowed to draw 30 mL of the aqueous media and the dispersed oil extracted with Dichloromethane (DCM). Then quantified with UV-VIS (PC-based Double Beam Spectrophotometer 2202, Systronics) at an absorbance of 340, 370, and 400 nm.

3. RESULT AND DISCUSSIONS

3.1 Effect of Interfacial Tension on DE (%) of Lecithin Blends (LT 85 and LT 80)

Interfacial tension measurements of Lecithin / Tween derivatives dissolved in ethanol showed an interfacial tension reduction capability. The combination of Lecithin with Tweens resulted in a significant reduction in interfacial tension and high dispersion efficiency (Efavi *et al*, 2017). Adding salts to the system can alter the distribution of surfactants at the interface owing to electrostatic effects and consequently IFT values changes. In addition, as the salinity increases above 3000 ppm, the IFT insignificantly decreases again. This observed trend could be related to the packing efficiency of surfactants occurring at the solution interface that enhances the capability of the surfactants for IFT reduction (Maliq *et al*, 2015). "**Figure. 1"** and "**Figure 2"** display the interfacial tension of Lecithin blends (LT 80 and LT85). There is a relation between interfacial tension, Hydrophilic-Lipophilic balance, Lecithin-Tween ratio with dispersant effectiveness. The ratio of Lecithin-Tween decides the Hydrophilic-Lipophilic balance of certain blends, as Tween 85 (HLB 11) and Tween 80 (HLB 15) have different HLB values. (Jin *et al;*2019, Nyakson *et al;* 2015, Maliq, 2015)

3.2 Effect of salts on DE (%) of Lecithin blends (LT 85 and LT 80)

Overall, it indicated that LT 80 and LT 85 have the highest (90%) and significant ($p < 0.05$) dispersant effectiveness in artificial sea salt. Magnesium salts increase dispersant effectiveness as compared to Sodium salts and that were significant ($p < 0.05$). In Sodium salts, Sodium chloride proceeds effectiveness higher ($p < 0.05$) as compared to Sodium sulfate and Sodium benzoate. Sodium benzoate significantly reduced the effectiveness of applied blended dispersants. However, Magnesium sulfate has inclined ($p < 0.05$) the effectiveness as compared to Magnesium chloride.

Table 1: TWO-WAY ANOVA for Effect of Surfactants used on DE (%) in Various Salt Solutions

Dependent Variable: Dispersant Effectiveness (%)							
Surfactant	**Salt Moieties**		**Mean Difference (I-J)**	**Std. Error**	**Sig.[b]**	**95% Confidence Interval for Difference[b]**	
						Lower Bound	**Upper Bound**
L/T - 85	Artificial Sea Salt	NaCl	7.555*	.938	**.000**	4.785	10.326
		MgCl2	17.307*	.938	**.000**	14.536	20.077
		Na2SO4	21.403*	.938	**.000**	18.633	24.174
		MgSO4	4.818*	.938	**.000**	2.048	7.589
		Na-benzoate	22.149*	.938	**.000**	19.378	24.919

L/T - 80	Artificial Sea Salt	NaCl	3.629*	.938	**.002**	.858	6.399
		MgCl2	12.474*	.938	**.000**	9.703	15.244
		Na2SO4	13.897*	.938	**.000**	11.126	16.667
		MgSO4	4.079*	.938	**.000**	1.309	6.850
		Na-benzoate	21.387*	.938	**.000**	18.616	24.157
Based on estimated marginal means							
*. The mean difference is significant at the .05 level.							
b. Adjustment for multiple comparisons: Bonferroni.							

3.3 Effect of Temperature and Salinity on DE (%) of Lecithin Blends (L/T-85 and L/T-80)

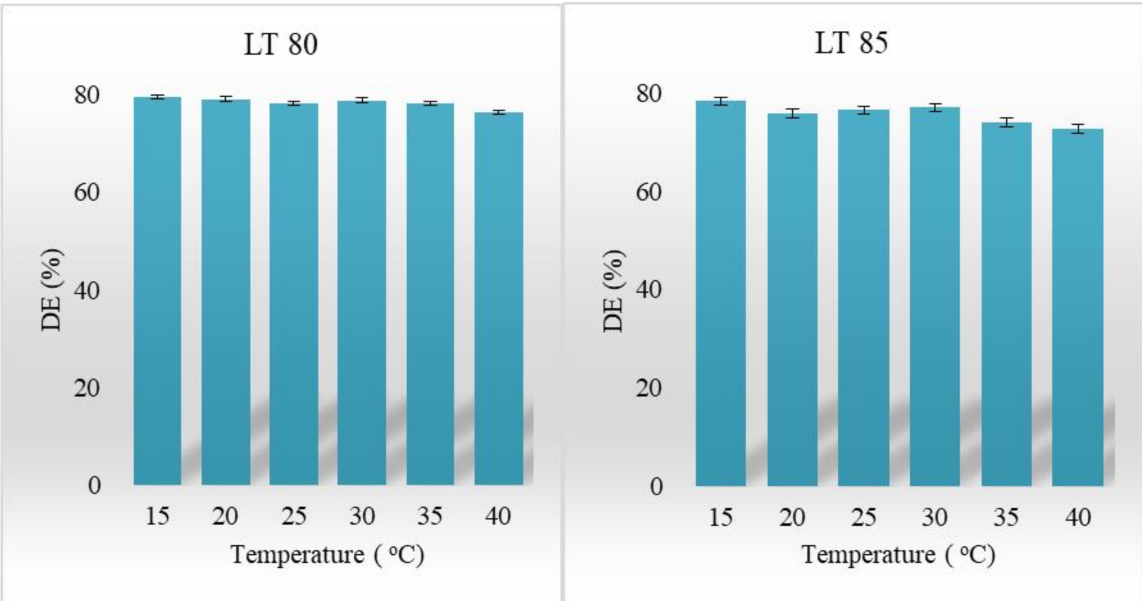

Figure 3: Dispersion Effectiveness (%) of Lecithin Blends (LT 80 and LT 85) at the Various Temperature Range

Temperature and salinity are resulting key factors to decide the dispersion effectiveness of various dispersants when the dispersion of oil in water occurs. In this study, at 15°C DE of both the blends have higher points. However, as temperature increases, DE decreases, this trend was the opposite for Lecithin blends. At lower temperatures, its effectiveness was more in percentage.

In this experiment, it indicated that, as salinity shifted towards the higher value, DE also moved to up ($p < 0.05$). Moreover, this relation continues with all the other applied salts. The effectiveness of dispersants can be modified with the oil type, surfactant, mixing energies, temperature, and particulars of the dispersion medium such as salinity, the content of specific ions) (Venkatraman *et al*, 2013; Powell *et al*, 2016).

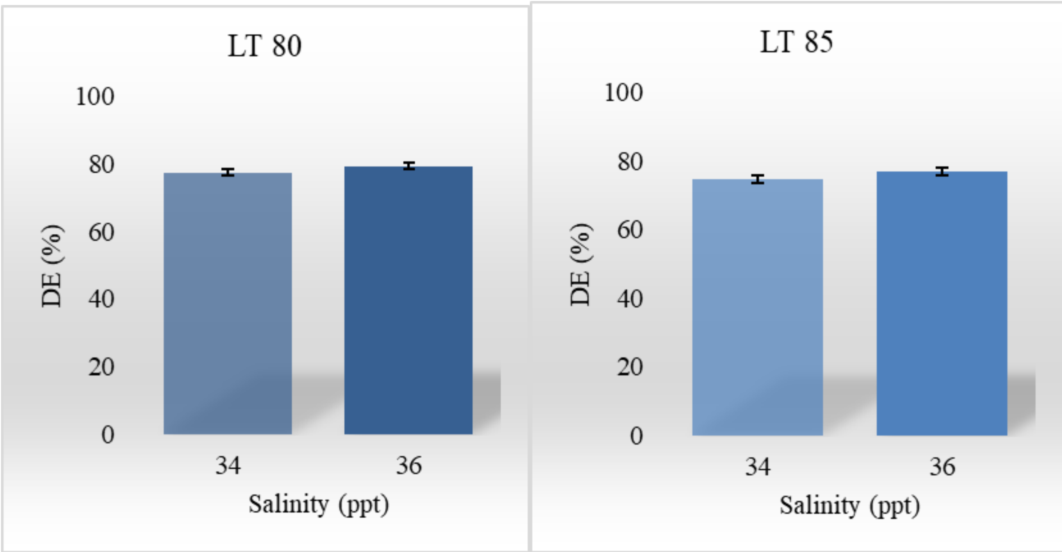

Figure 4: Dispersion Effectiveness (%) of Lecithin Blends (LT 80 and LT 85) at Different Salinity

Moreover, at the oil-water interface, the adsorption of hydroxyl ions is promoted by conferring a charge of nonionic surfactant (Kasemset *et al*, 2017; Marinova *et al*, 1996). FT-IR confirms these results by having Hydroxyl stretching and phospholipids functional groups present were recorded. "**Figure 5" and "Figure 6"**. A droplet-droplet electrostatic repulsion is reduced when salts present in the continuous phase lead to a decrease in the Debye length due to charge screening (Zhu *et al*, 2017; Tummons *et al*, 2017), which favors droplet coalescence (Tummons *et al*, 2017; Powell *et al*, 2017). Due to salting out of the surfactant, a decrease in the interfacial tension counteracted the effect of salt induction. This is the reason for making droplets more stable and less likely to coalesce in the dissolved phase for an oil-water interface (Nyakson *et al*, 2016).

4. CONCLUSIONS

This experiment adds to a growing corpus of research showing Interfacial tension of Lecithin Tween derivatives dissolved in ethanol showed reduction capability. The potential of dispersants formulated with lecithin (LT 80 and LT 85) to replace the traditional liquid chemical dispersant formulations. In addition, different salts affected the stability of lecithin blends differently. The practical effect of the salts on oil spill remediation using the baffled flask test confirmed that the salts have a significant ($p < 0.05$) effect on the dispersion effectiveness of lecithin blends with Tweens. In Artificial sea salt, NaCl, $MgSO_4$ solution DE was on significant peak positions ($p < 0.05$) than $MgCl_2$, Na_2SO_4. In Sodium benzoate, both lecithin-tween blends recorded dispersion effectiveness below the average level (around 65%). In conclusion, it would appear that the stability of Lecithin blends is more in dispersion effectiveness of High-Density Oil. In addition, the salts present in the marine environment will be denatured the effect of the oil.

5. ACKNOWLEDGEMENTS

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Supplementary Page

Figure 1 and 2: Interfacial Tension (IFT) of LT 80 and LT 85 by Pendant Drop Tensiometer

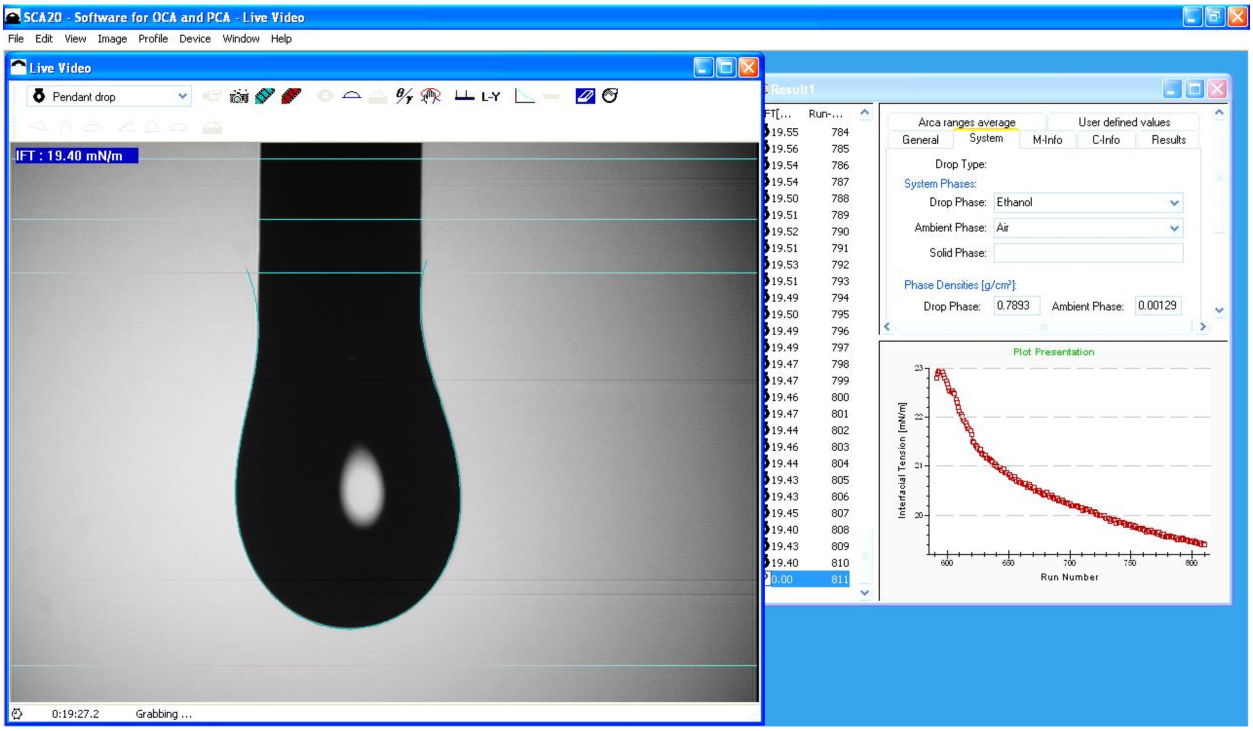

Figure 1

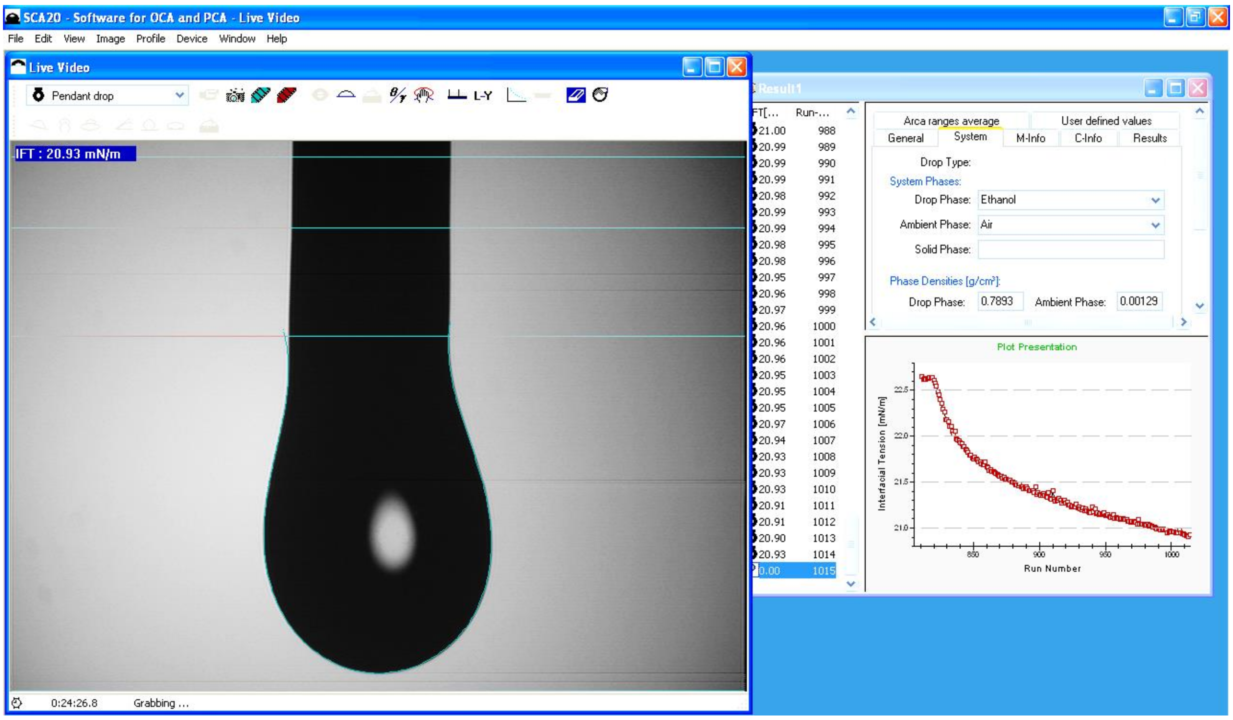

Figure 2

Figure 5 and 6: FT-IR of LT 80 and LT 85

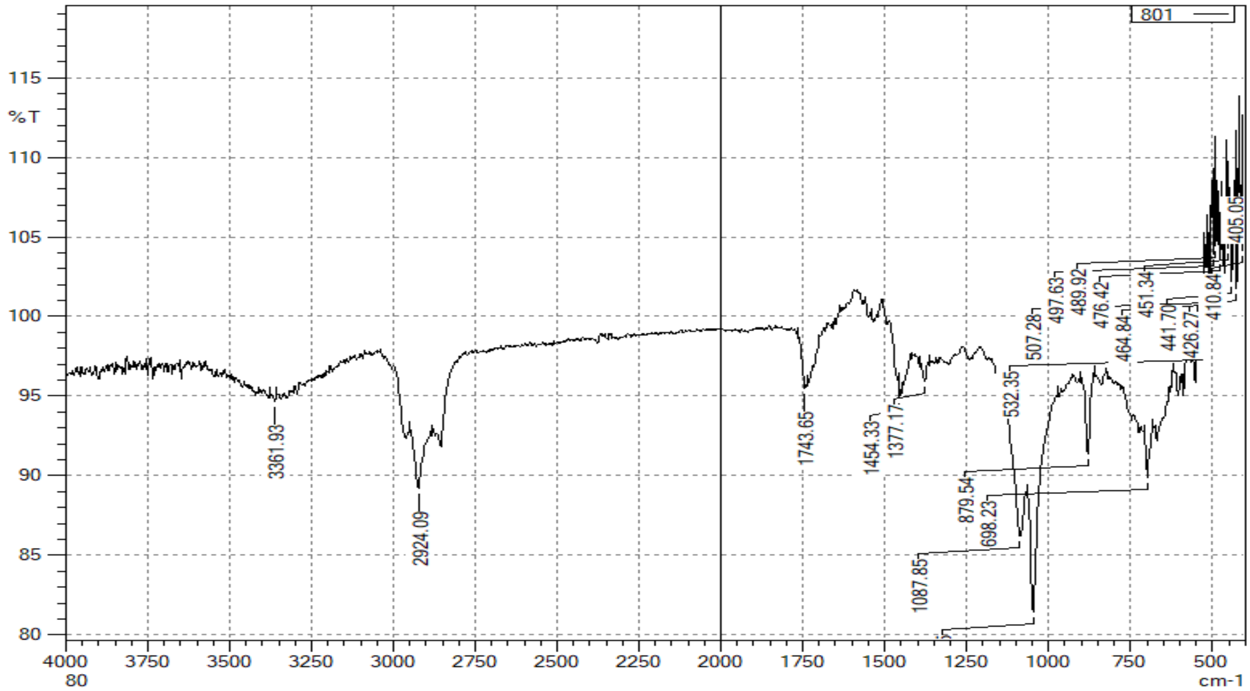

Figure 5

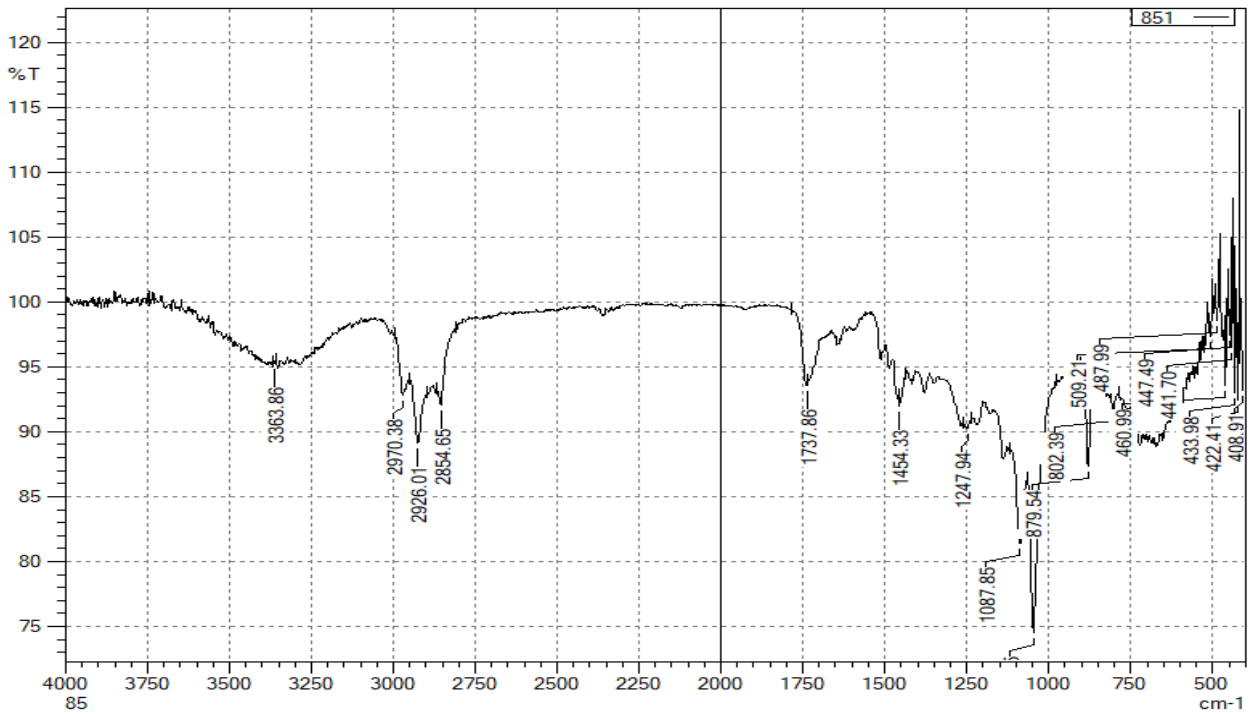

Figure 6